Migration of Bidentate Anionic Ligands in Binuclear Compounds derived from 1,2-Bis(imino)propyl–Palladium(II) Complexes

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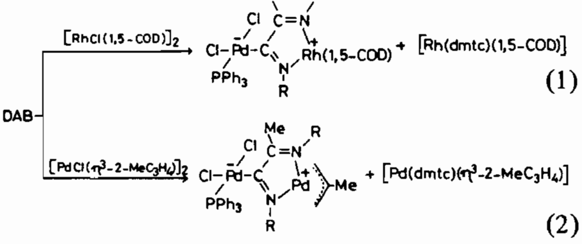
The complexes $[Pd(A–B)\{C(=NR)CMe=NR\}(PPh_3)]$ *(I; A–B = 2,4-pentanedionate, N-methylsalicylaldiminate, pyrrole-2-N-methylaldiminate; R =* p-C_6H_4OMe*) react with* 'MCl_2' *(*'MCl_2' *=* $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $[PdCl_2(N{\equiv}CMe)_2]$, $K[PtCl_3(CH_2{=}CH_2)]$*) to give either the binuclear adducts* $[(PPh_3)(A–B)Pd\{C(=\overline{NR)CMe=NR}\}MCl_2]$ *(II) or the zwitterionic isomers* $[(PPh_3)Cl_2Pd\{C(=\overline{NR)CMe=NR}\}\overline{M}(A–B)]$ *(III) depending on the nature of the metal M and of the anionic ligand A–B. The formation of products III is accounted for in terms of an intramolecular migration of ligands between the two metal centers Pd and M of the initially formed* MCl_2 *adducts II.*

Introduction

In the course of our studies on the coordination abilities of the complex $[Pd(dmtc)\{C(=NR)CMe=NR\}(PPh_3)]$ (dmtc = dimethyldithiocarbamate; R = p-C_6H_4OMe, DAB), we have observed that in some reactions the bidentate anionic ligand migrates from palladium to other metal centers in the system [1–3]:



(1)

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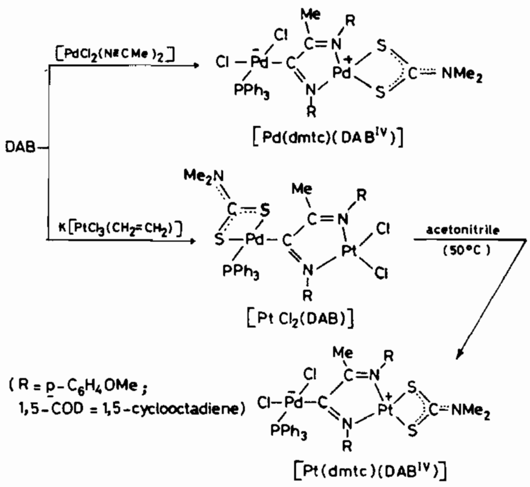

(3)

(4)

The mechanism of reaction 2 has been elucidated by a kinetic investigation [2]. Reactions 3 and 4, however, proved to be too fast and too slow respectively, to be studied kinetically by conventional spectrophotometric techniques. In order to gain more information about the factors affecting ligand migration reactions of this type and, possibly, about their mechanism, we have prepared new 1,2-bis(imino)propyl–palladium(II) complexes with different anionic bidentate ligands and studied their interactions with a variety of transition metal chlorides.

Experimental

The complexes $[PdCl_2(N{\equiv}CMe)_2]$ and $K[PtCl_3(CH_2{=}CH_2)]$ were prepared by standard methods. The 1,2-bis(imino)propyl derivatives [Pd(dmtc)-

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{C(=NR)CMe=NR}(PPh$_3$)] (DAB), and *trans*-[PdCl{C(=NR)CMe=NR}(PPh$_3$)$_2$] (R = *p*-C$_6$H$_4$OMe) were prepared and purified by published procedures [3, 4]. The thallous salts of 2,4-pentanedione (Tl[acac]), N-methylsalicylaldimine (Tl[Mesal]) and pyrrole-2-N-methylaldimine (Tl[Mepyr]) were obtained in almost quantitative yields from the reaction of the organic substrate with an equimolar amount of TlOEt in diethyl ether or n-hexane. All other chemicals and solvents were reagent grade, and were used without further purification.

Preparation of the Complexes [Pd(A–B){C(=NR)CMe=NR}(PPh$_3$)] (R = p-C$_6$H$_4$OMe; A–B = acac, DAB^I; A–B = Mesal, DAB^{II}; A–B = Mepyr, DAB^{III})

a) The complex *trans*-[PdCl{C(=NR)CMe=NR}(PPh$_3$)$_2$] (1.90 g, 2 mmol) dissolved in *ca.* 100 ml of 1,2-dichloroethane was reacted with Tl[acac] (0.91 g, 3 mmol). After 6 hr stirring in the dark, the reaction mixture was treated with charcoal and filtered. The clear yellow solution was concentrated to small volume and the product, DAB^I, was precipitated with n-hexane/diethyl ether (2/1, v/v). This compound was purified by two successive re-precipitations from the same solvents (yield 1.32 g, 88% based on the theoretical amount).

b) The complexes DAB^{II} and DAB^{III} were prepared by a similar method using Tl[Mesal] and Tl[Mepyr] respectively, and benzene as solvent. The final products were precipitated by addition of n-pentane and purified by two successive re-precipitations from benzene/n-pentane mixtures (yield 77%, DAB^{II}; 71%, DAB^{III}).

Reactions of DAB with MCl$_2$ (M = Co, Ni, Cu)

a) A solution of the ligand DAB (0.385 g, 0.5 mmol) in CH$_2$Cl$_2$ (50 ml) was added dropwise to a stirred solution of anhydrous CoCl$_2$ (0.065 g, 0.5 mmol) in anhydrous methanol (10 ml). After 30 min, the mixture was treated with charcoal and filtered. The clear solution was evaporated at reduced pressure until the product began to precipitate. The precipitation was completed by addition of diethyl ether. The binuclear complex [CoCl$_2$(DAB)] was purified by re-precipitation from the same solvents (yield 0.40 g, 89%). This compound was characterized by IR spectra [$\nu(\mathrm{C}\cdots\mathrm{N})_{\mathrm{dmtc}}$ = 1542 s; ν(Co–Cl) = 350 ms, 333 m; ν(Pd–S) = 370 m, cm^{-1}], electronic spectra (see Fig. 3), magnetic moment measurements (μ_{eff} = 4.58 B.M. for a 10^{-2} *M* CH$_2$Cl$_2$ solution at 22 °C), elemental analysis and molecular weight (Found: C, 50.4; H, 4.3; N, 4.5; Cl, 8.0; Mol. weight, 923. Calcd. for C$_{38}$H$_{38}$Cl$_2$N$_3$O$_2$PS$_2$CoPd: C, 50.70; H, 4.25; N, 4.67; Cl, 7.88; Mol. weight, 900.0).

b) The reactions with M = Ni or Cu were carried out as described above and gave a mixture of products which proved difficult to separate and characterize.

Reactions of DAB^I with MCl$_2$ (M = Co, Ni, Cu, Zn)

The ligand DAB^I was reacted with MCl$_2$ in the same way as described for the DAB/CoCl$_2$ system to yield the zwitterionic binuclear derivatives [M(acac)(DAB^{IV})] (M = Co, yield 73%; Ni, 70%; Cu, 89%).

For M = Zn, a mixture of untractable products was obtained.

Reactions of DAB^{II} and DAB^{III} with MCl$_2$ (M = Co, Ni, Cu, Zn)

The same procedure reported above for the DAB/CoCl$_2$ reaction was followed. Only for M = Zn was it possible to isolate the adducts [ZnCl$_2$(DAB^{II})] and [ZnCl$_2$(DAB^{III})] in 71 and 92% yield, respectively. In the other cases, the reaction gave a mixture of various products which could not be isolated in a satisfactorily pure state. For the system DAB^{II}/CuCl$_2$, the mother liquor, resulting from the precipitation of the insoluble materials upon addition of diethyl ether, was stored overnight at 0 °C yielding a small amount (0.03 g) of a green solid, which was identified as [Cu(Mesal)$_2$] from elemental analysis (Found: C, 57.8; H, 4.9; N, 7.4. Calcd. for C$_{16}$H$_{16}$N$_2$O$_2$Cu: C, 57.91; H, 4.86; N, 8.44) and from comparison of the IR spectrum [ν(C=N) = 1630 cm^{-1}] with that of an authentic sample prepared by literature methods [5].

Reactions of DAB^I, DAB^{II} and DAB^{III} with [PdCl$_2$(N≡CMe)$_2$]

The 1,2-bis(imino)propyl derivative (0.5 mmol) in CH$_2$Cl$_2$ (50 ml) reacted immediately with [PdCl$_2$(N≡CMe)$_2$] (0.13 g, 0.5 mmol) to give a red-orange mixture, which was stirred for 30 min, treated with charcoal and filtered. The clear solution was concentrated to small volume and the product precipitated by addition of diethyl ether. The crude compound was purified by re-precipitation from the same solvents (yield 72% for [Pd(acac)(DAB^{IV})]; 95% for [PdCl$_2$(DAB^{II})]; 87% for [PdCl$_2$(DAB^{III})]).

Reactions of DAB^I, DAB^{II} and DAB^{III} with K[PtCl$_3$(CH$_2$=CH$_2$)]

These reactions were carried out as described in a previous paper [3] for the preparation of [PtCl$_2$(DAB)] (yields 75–80%).

Reaction of [Cu(acac)(DAB^{IV})] with 2,2'-Bipyridine (bipy)

The complex [Cu(acac)(DAB^{IV})] (0.44 g, 0.5 mmol) in CH$_2$Cl$_2$ (7 ml) was treated with an excess of bipy (0.31 g, 2 mmol). A turquoise compound began to precipitate within a few seconds. After 5 min stirring, the precipitation was completed by addition of diethyl ether (10 ml). The product [Cu(acac)(bipy)]Cl (0.15 g) was filtered off and the red-orange mother liquor was reacted with PPh$_3$

(0.26 g, 1 mmol) to give a yellow solution, which was concentrated to small volume. Upon addition of diethyl ether, the complex *trans*-[PdCl{C(=NR)-CMe=NR}(PPh$_3$)$_2$] (0.46 g) was obtained as a yellow microcrystalline solid.

Reaction of [ZnCl$_2$(DAB^{II})] with Bipy

When bipy (0.25 g, 1.6 mmol) was added to a solution of [ZnCl$_2$(DAB^{II})] (0.37 g, 0.4 mmol) in CH$_2$Cl$_2$ (8 ml), a yellow compound began to precipitate. After 10 min the precipitation was completed by adding diethyl ether (10 ml). The product (0.10 g) was identified as [ZnCl$_2$(bipy)] on the basis of its IR spectrum [ν(Zn–Cl) = 334 and 325 cm^{-1}] [6].

The mother liquor was concentrated to small volume and n-hexane was added to give a yellow precipitate (0.28 g), the IR and ^{1}H NMR spectra of which were identical to those of DAB^{II}.

Reaction of [PtCl$_2$(DAB^{II})] with 1,2-Bis(diphenylphosphino)ethane (dppe)

The complex [PtCl$_2$(DAB^{II})] (0.21 g, 0.2 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with dppe (0.08 g, 0.2 mmol). The colour of the reaction mixture changed immediately from deep-red to yellow-orange. Dropwise addition of diethyl ether gave a yellow precipitate of [PtCl$_2$(dppe)] (0.10 g) [ν(Pt–Cl) = 313 and 290 cm^{-1}]. The mother liquor was worked up as described for the reaction of [ZnCl$_2$(DAB^{II})] with bipy to give a yellow solid as a mixture of [PtCl$_2$(dppe)] and DAB^{II}, from which the pure ligand DAB^{II} (0.12 g) could be separated by re-precipitation from benzene/n-pentane.

Reaction of [PdCl$_2$(DAB^{III})] with PPh$_3$

Upon addition of PPh$_3$ (0.13 g, 0.5 mmol) to [PdCl$_2$(DAB^{III})] (0.23 g, 0.25 mmol) in CH$_2$Cl$_2$ (7 ml) an immediate reaction took place with formation of a yellow precipitate. After 10 min stirring, the precipitation was completed by adding diethyl ether (7 ml). The product was identified as *trans*-[PdCl$_2$(PPh$_3$)$_2$] from its IR spectrum (yield 0.16 g). The mother liquor was concentrated to small volume and n-hexane was added for the precipitation of the free DAB^{III} ligand (0.17 g).

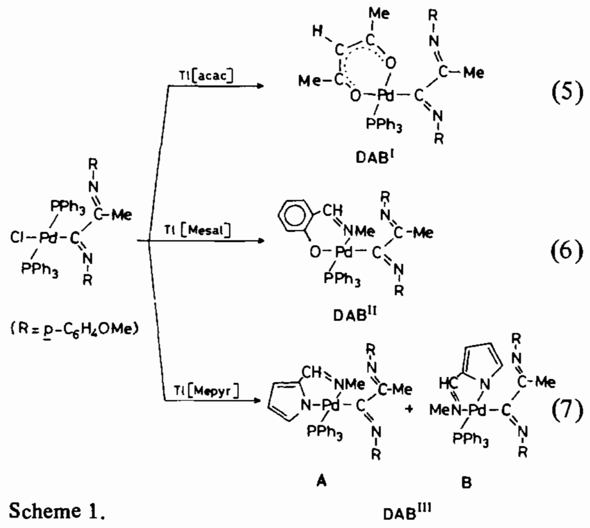
Physical Measurements

Molecular weights were determined in 1,2-dichloroethane at 37 °C with a Knauer osmometer. The conductivity measurements were carried out with a Philips PR9500 bridge at 20 °C. The ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer with tetramethylsilane (TMS) as internal standard or on a Varian FT80 A instrument with dichloromethane-d$_2$ as internal standard. Electronic spectra in solution were recorded with a Cary model 14 recording spectrophotometer in the range 2000–500 nm and with a Bausch-Lomb Spectronic 210 UV instrument in the range 600–250 nm at 25 °C. Magnetic moments in the solid were determined with a Bruker Magnet BM6 instrument, whereas those in 10^{-2} M CH$_2$Cl$_2$ solution were measured by published methods [7]. Infrared spectra were recorded with a Perkin-Elmer 597 instrument, using hexachlorobutadiene mulls in the range 4000–1300 cm^{-1} and Nujol mulls in the range 1700–250 cm^{-1}. The EPR spectra were obtained with a Varian E-9 instrument in frozen CH$_2$Cl$_2$ solutions at liquid nitrogen temperature. (We thank Dr. A. Bencini of ISSECC, C.N.R., Florence, for the latter measurements).

Results and Discussion

Preparation of the 1,2-Bis(imino)propyl–palladium(II) Complexes

These complexes have been prepared by substitution reaction at the palladium center of *trans*-[PdCl{C(=NR)CMe=NR}(PPh$_3$)$_2$] (R = p-C$_6$H$_4$OMe) by thallous salts of the bidentate anionic ligands (Scheme 1).



Scheme 1.

The set of bidentate ligands has been chosen in order to give palladium adducts of different stabilities, owing to the different donor atoms and size of the chelate ring.

The complexes DAB^I, DAB^{II} and DAB^{III} are monomeric in 1,2-dichloroethane (see Table I) and non-conducting in more polar solvents, such as methanol and acetonitrile, where they show no tendency towards dissociation of the bidentate anions even at low concentrations (Lambert–Beer's law is obeyed down to 10^{-5} M solutions).

The formulation is mainly based on IR and ^{1}H NMR spectral evidence (Tables II and III) and on chemical reactivity (see further). The 1,2-bis(imino)-

TABLE I. Analytical and Physical Data.

Compound	Colour	M.P. (°C)[a]	C[b]	H	N	Cl	M.W.[b]	μ_{eff}[c] (B.M.)
$[DAB^{I}]$	yellow	179	63.7	5.4	3.8		772	
			(64.13)	(5.25)	(3.74)		(749.1)	
$[Co(acac)(DAB^{IV})]$	yellow-brown	177	54.6	4.5	3.1	8.1	d	4.34
			(54.66)	(4.47)	(3.19)	(8.07)	(878.9)	[3.75]
$[Ni(acac)(DAB^{IV})]$	yellow-brown	203	55.2	4.4	3.1	7.7	d	3.22
			(54.67)	(4.47)	(3.19)	(8.07)	(878.7)	[2.05]
$[Cu(acac)(DAB^{IV})]$	olive-green	168	54.2	4.3	3.1	8.1	865	
			(54.37)	(4.45)	(3.17)	(8.02)	(883.5)	[1.76]
$[Cu(acac)(bipy)]Cl$[e]	turquoise	186	50.9	4.3	7.8	10.3		[1.71]
			(50.85)	(4.27)	(7.91)	(10.01)		
$[Pd(acac)(DAB^{IV})]$	orange	176	51.3	4.2	2.9	7.8	928	
			(51.86)	(4.24)	(3.02)	(7.65)	(926.4)	
$[PtCl_2(DAB^{I})]$	red-brown	186	46.9	4.0	2.7	7.0	1064	
			(47.33)	(3.87)	(2.76)	(6.98)	(1015.1)	
DAB^{II}	yellow	160	65.9	5.1	5.3		790	
			(65.86)	(5.14)	(5.36)		(784.15)	
$[ZnCl_2(DAB^{II})]$	deep yellow	166	56.0	4.3	4.6	7.8	915	
			(56.11)	(4.38)	(4.57)	(7.70)	(920.4)	
$[PdCl_2(DAB^{II})]$	yellow-orange	192	53.4	4.0	4.3	7.5	f	
			(53.71)	(4.19)	(4.37)	(7.37)		
$[PtCl_2(DAB^{II})]$	orange	189	49.4	3.9	3.9	6.5	1040	
			(49.18)	(3.84)	(4.00)	(6.75)	(1050.1)	
DAB^{III}	yellow	162	65.3	4.9	7.4		752	
			(65.04)	(5.19)	(7.40)		(757.1)	
$[ZnCl_2(DAB^{III})]$	deep yellow	216	54.8	4.3	6.1	8.1	903	
			(55.12)	(4.40)	(6.27)	(7.94)	(893.4)	
$[PdCl_2(DAB^{III})]$	yellow-orange	181	52.0	4.1	5.9	7.8	998	
			(52.70)	(4.21)	(6.00)	(7.59)	(934.4)	
$[PtCl_2(DAB^{III})]$	orange	196	48.0	3.8	5.5	6.9	1079	
			(48.13)	(3.84)	(5.48)	(6.93)	(1023.1)	

[a] Uncorrected values: all compounds decompose on melting. [b] Calcd. values in parenthesis. [c] The figures in square brackets refer to magnetic moments measured in CH_2Cl_2 solutions 10^{-2} M at 22 °C; the magnetic moments in the solid have been measured at 20 °C. [d] See text. [e] $\Lambda_M = 86.2$ ohm^{-1} cm^2 mol^{-1} for a methanol solution 10^{-3} M at 20 °C. [f] Scarcely soluble in 1,2-dichloroethane.

propyl group is characterized by two ν(C=N) stretching vibrations in the range 1622–1544 cm^{-1}, indicating that the imino nitrogen atoms are not involved in coordination [4, 8]. Furthermore, the DAB^{I} derivative shows a ν(Pd–O) band at 430 cm^{-1} and very intense ν(C⋯⋯O) and ν(C⋯⋯C) at 1585, 1573, 1394 and 1520, 1297 cm^{-1} respectively, typical of an oxygen-bound acac group [9]. This type of coordination is also supported by the ^{1}H NMR spectrum, in which the acac methyl protons appear as two distinct singlets (1/1 integration ratio), suggesting a rather rigid configuration for the chelate ring in DAB^{I}. The IR spectra of DAB^{II} and DAB^{III} show also a strong ν(C=N) band at 1620 and 1592 cm^{-1} of the bidentate Mesal and Mepyr anions, respectively.

Due to the asymmetric nature of the chelate ligands, DAB^{II} and DAB^{III} may exist as two geometrical isomers. The presence of such isomers (in a molar ratio 1/1.3) is clearly indicated in the ^{1}H NMR spectrum of DAB^{III} by the occurrence of two singlets for each of δ(OMe), δ(C-Me) and δ(N-Me) signals. This doubling of signals cannot result from different conformations of the 1,2-bis(imino)propyl group, because it is still present in the adducts $[MCl_2(DAB)^{III}]$ (M = Zn, Pd, Pt), where the α-diimino group is forced by chelation to assume a configuration with *'cis'* C=N bonds (see Table III and Fig. 4). On the other hand, in all the previously prepared complexes of this type, as well as in DAB^{I} and DAB^{II}, the 1,2-bis(imino)alkyl moiety was found to assume in solution only one of its possible configurations, which very likely corresponds to that of organic α-diimines [10] and to that observed in the solid for the complex *trans*-$[PdCl\{C(=NR)CMe=NR\}(PPh_3)_2]$ (R = *p*-C_6H_4OMe) where the planar N=C–

TABLE II. Characteristic IR Bands (cm^{-1}).

Compound	ν(C=N)^a	ν(C=N)^b	ν(C$\underline{\cdots}$O)^c	ν(C$\underline{\cdots}$C)^c	ν(Pd–Cl)^d	ν(M–Cl)^e	Other bands
DAB^I	1622s; 1551s		1585s; 1573s; 1394s	1520s; 1297s			430m[ν(Pd–O)]
[Co(acac)(DAB^{IV})]	f		1580vs; 1379s	1517s; 1296ms	298ms; 278sh		428m[ν(Co–O)]
[Ni(acac)(DAB^{IV})]	f		1600vs,br; 1393s	1517s; 1296m	295ms; 284m		432m[ν(Ni–O)]
[Cu(acac)(DAB^{IV})]	f		1588vs; 1380s	1518s; 1295m	296ms; 275m		458m[ν(Cu–O)]
[Cu(acac)(bipy)]Cl			1585vs,br; 1389s	1513s; 1282ms or 1276ms			447ms ν(Cu–O)
[Pd(acac)(DAB^{IV})]	f		1561s; 1370s	1520s; 1297ms	296m; 280m		463m[ν(Pd–O)]
[PtCl$_2$(DAB^I)]	f		1577s; 1565s 1384s	1518s; 1301m		343ms; 344sh	443m[ν(Pd–O)]
DAB^{II}	1620vs; 1544ms	1620vs					
[ZnCl$_2$(DAB^{II})]	f	1621vs				342s; 312ms	
[PdCl$_2$(DAB^{II})]	f	1622vs				353ms; 335ms	
[PtCl$_2$(DAB^{II})]	f	1626vs				348ms; 335sh	
DAB^{III}	1620ms; 1565sh	1592vs					
[ZnCl$_2$(DAB^{III})]	1546m	1592vs				346s; 311ms	
[PdCl$_2$(DAB^{III})]	f	1597vs				350ms; 336ms	
[PtCl$_2$(DAB^{III})]	f	1598vs				345ms; 335ms	

[a] Vibrations of the 1,2-bis(imino)propyl group. [b] Vibrations of the anionic ligands Mesal or Mepyr. [c] Vibrations of the acac group. [d] Bands of the DAB^{IV} ligand. [e] Bands of the coordinated MCl$_2$ unit. [f] The ν(C=N) bands of the coordinated 1,2-bis(imino)propyl group cannot be observed because of the intense absorptions of the p-C$_6$H$_4$OMe phenyl rings (around 1600 and 1500 cm^{-1}) and of the ligands acac, Mesal or Mepyr (in the range 1600–1500 cm^{-1}).

TABLE 111. Selected ^{1}H NMR Spectral Data.[a]

Compound	1,2-Bis(imino)propyl Group		Bidentate Anionic Ligand				Solvent
	O-Me	C-Me	N=C-H	>C–H	N-Me	C-Me	
DAB^{I}	3.79S 3.74S	1.88S or 1.83S		5.15S		1.88S or 1.83S 1.45S	$CDCl_3$
$[\mathrm{Pd(acac)(DAB^{IV})}]$	3.89S 3.79S	2.88S		5.15S		1.63S[b]	$CDCl_3$
$[\mathrm{PtCl_2(DAB^{I})}]$	3.81S 3.78S	2.09T ^4J(Pt–H) = 9.0		5.34S		2.04S 1.51S	$CDCl_3$
DAB^{II}	3.78S 3.77S	1.75S	7.87D_Q ^4J(P–H) = 11.3		3.35D_D ^4J(H–H) = 1.3 ^4J(P–H) = 1.8		CD_2Cl_2
$[\mathrm{ZnCl_2(DAB^{II})}]$	3.76S 3.74S	2.72S	7.99D_Q ^4J(P–H) = 11.4		3.31D_D ^4J(H–H) = 1.3 ^4J(P–H) = 2.0		CD_2Cl_2
$[\mathrm{PdCl_2(DAB^{II})}]$	3.77S 3.75S	2.48S	7.93D_Q ^4J(P–H) = 12.3		3.55D_D ^4J(H–H) = 1.1 ^4J(P–H) = 2.2		CD_2Cl_2
$[\mathrm{PtCl_2(DAB^{II})}]$	3.78S 3.75S	2.09T ^4J(Pt–H) = 9.0	7.92D_Q ^4J(P–H) = 13.5		3.44D_D ^4J(H–H) = 1.1 ^4J(P–H) = 2.2		CD_2Cl_2
DAB^{III}[d]	3.82S 3.81S 3.80S 3.79S	1.86S[e] 1.79S[f]	7.73D_Q[f] ^4J(P–H) = 8.0 m[c,e]		3.22D_D[f] ^4J(H–H) = 1.1 ^4J(P–H) = 2.3 2.25M ^4J(H–H) ~ 1 ^4J(P–H) ~ 0.7		CD_2Cl_2
$[\mathrm{ZnCl_2(DAB^{III})}]$[d]	3.84S 3.80S	2.77S[f] 2.75S[e]	m[c]		3.20D_D[f] ^4J(H–H) = 1.0 ^4J(P–H) = 3.1 2.33M[e,g] ^4J(H–H) ~ 1 ^4J(P–H) ~1		CD_2Cl_2
$[\mathrm{PdCl_2(DAB^{III})}]$[d]	3.82S 3.79S 3.77S	2.65S[f] 2.45S[e]	m[c]		3.42D_D[f] ^4J(H–H) ~ 1 ^4J(P–H) = 3.0 2.17M[e,g]		CD_2Cl_2
$[\mathrm{PtCl_2(DAB^{III})}]$[d]	3.83S 3.80S 3.78S	2.08T[e] 2.06T[f] ^4J(Pt–H) = 9.0	m[c]		3.32D_D[f] ^4J(H–H) = 1.0 ^4J(P–H) = 3.3 2.18M[e,g] ^4J(H–H) ~ 1 ^4J(P–H) ~ 1		CD_2Cl_2

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[a] Spectra recorded at 30 °C; δ values in ppm from TMS; S = singlet, D_D = doublet of doublets, D_Q = doublet of quartets, T = triplet, M = multiplet; satisfactory integration values have been obtained. [b] The integration of this signal corresponds to six protons. [c] Masked by the intense phenyl proton resonances. [d] Two geometrical isomers. [e] Signals of the isomer B (see text). [f] Signal of the isomer A. [g] Poorly resolved multiplet.

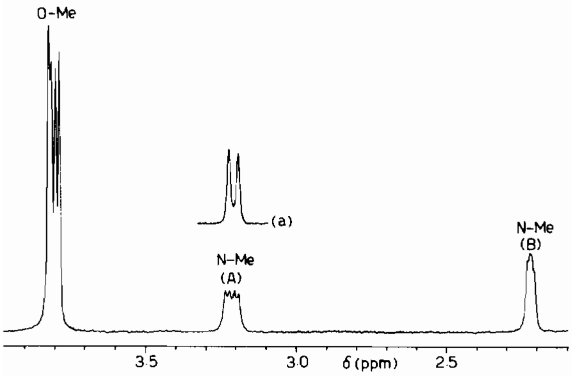


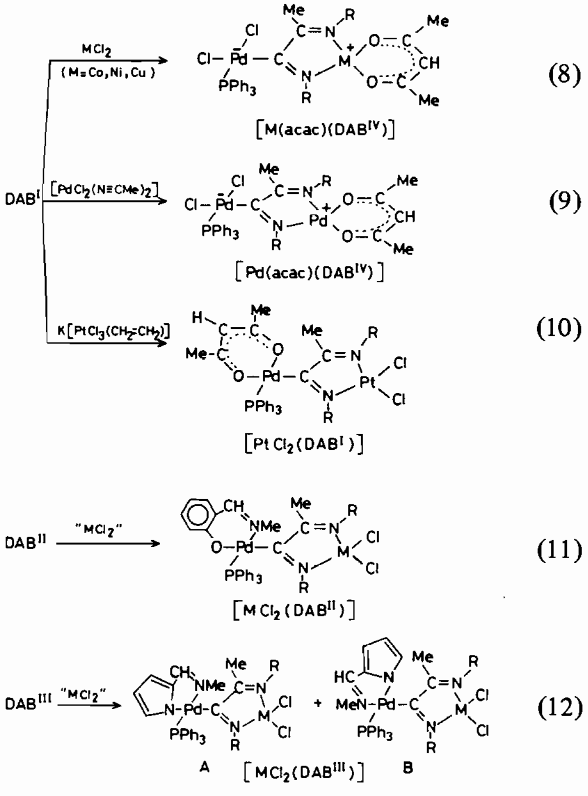
Fig. 1. ^1H NMR spectrum of DAB^{III} in the range 2.0–4.0 ppm; (A) signal of isomer A, (B) signal if isomer B. a) δ(N-Me) signal upon irradiation at 7.73 ppm.

C=N unit has a *'trans'* arrangement of the C=N double bonds with *anti* nitrogen substituents [8]. In DAB^{III} the structures A and B are assigned to the minor and major isomers, respectively, on the basis of the different $^4J(P-H)$ coupling constants between the PPh_3 and –HC=NMe groups depending on whether they are *trans* (A, $^4J(P-H)$ = 2.3 and 8.0 Hz for the NMe and N=CH protons, respectively) or *cis* to each other (B, $^4J(P-H) \sim 0.7$ Hz for the NMe protons). It is well known that in square-planar complexes the coupling constants between *trans* ligands are generally greater than those between the same ligands in a *cis* configuration. As can be seen in Fig. 1, the δ(N-Me) signal of A appears as a doublet of doublets at 3.22 ppm because of the additional coupling with the N=CH proton, whereas δ(N-Me) of B occurs at higher field, 2.25 ppm, as a poorly-resolved multiplet resulting from extensive overlap of rather close signals, due to the small coupling constants with the ^{31}P nucleus of the *cis* PPh_3 ligand and with the N=CH proton [$^4J(H-H) \sim$ 1 Hz]. The assignment of δ(N-Me) and δ(N=CH) for isomer A is further confirmed by spin decoupling experiments. Upon irradiation at a frequency corresponding to 7.73 ppm, the δ(N-Me) signal appears as a doublet from which the $^4J(P-H)$ coupling constant can be easily measured. Conversely, a sharp doublet is also obtained for δ(N=CH) on irradiating at 3.22 ppm.

The complex DAB^{II} is present in solution with only one isomer, to which a structure of type A with the –HC=NMe group *trans* to PPh_3 is assigned on the basis of chemical shift and coupling constant considerations. In this case, the δ(N-Me) and δ(N=CH) signals occur at 3.35 [two overlapping doublets, $^4J(P-H)$ = 1.8 Hz] and 7.87 ppm [doublets of quartets, $^4J(P-H)$ = 11.3 Hz], respectively, *i.e.* with chemical shifts and $^4J(P-H)$ coupling constants rather close to those of isomer A of DAB^{III}. Also for DAB^{II}, the assignment of δ(N-Me) and δ(N=CH) signals was confirmed by spin decoupling tests.

Coordination Reactions

The coordination reactions of 1,2-bis(imino)-propyl derivatives with some transition metal chlorides are reported in Scheme 2.



("MCl_2" = $ZnCl_2$, $[PdCl_2(N\equiv CMe)_2]$, $K[PtCl_3(CH_2=CH_2)]$)

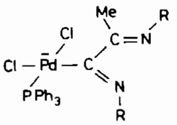
Scheme 2

All these reactions are very fast and yield binuclear complexes through chelation of the α-diimino moiety. In reactions 8 and 9, a fast migration of ancillary ligands between the Pd and M metal centers is also involved. The reaction of DAB^I with $ZnCl_2$ and those of DAB^{II} or DAB^{III} with MCl_2 (M = Co, Ni, Cu) gives a mixture of products difficult to isolate and characterize. In the latter systems some decomposition takes place, as can be inferred from the isolation of a small amount of $[Cu(Mesal)_2]$ in the $DAB^{II}/CuCl_2$ reaction mixture. In the reactions of DAB with MCl_2 (M = Co, Ni, Cu, Zn), well-defined 1/1 adducts $[MCl_2(DAB)]$ were obtained only for M = Co (see Experimental) and Zn [3].

In general, the binuclear derivatives are monomers in 1,2-dichloroethane, with the exception of $[M(acac)(DAB^{IV})]$ (M = Co, Ni), which are partially associated in solution. Their experimental molecular weights are significantly higher than those calculated for monomeric species and decrease with increasing dilution:

	Conc. (g/l)	Found
[Co(acac)(DAB^{IV})]	8.80	1251
(calcd. M.W., 878.9)	1.90	1143
[Ni(acac)(DAB^{IV})]	8.10	1136
(calcd. M.W., 878.7)	1.75	1005

The IR spectra of the zwitterionic complexes [M(acac)(DAB^{IV})] (M = Co, Ni, Cu, Pd) show two ν(Pd–Cl) bands in the ranges 298–295 and 284–275 cm^{-1} respectively, which are typical for the coordinated anionic ligand DAB^{IV} [11]:



DAB^{IV}

Furthermore, the chelate M(acac) unit is characterized by M–O stretching vibrations, the values of which follow the same order: ν(Pd–O) > ν(Cu–O) > ν(Ni–O) > ν(Co–O) as observed for the bis-chelate derivatives [M(acac)$_2$] [12]. The presence of DAB^{IV} in [Pd(acac)(DAB^{IV})] is also suggested by the low-field chemical shift (2.88 ppm) of the C-Me protons of the 1,2-bis(imino)propyl group [11]. An identical δ(C-Me) value has been reported for the structurally related compound [Pd(dmtc)(DAB^{IV})] [3]. In the ^{1}H NMR spectrum of [Pd(acac)(DAB^{IV})], the acac methyl protons resonate at *ca.* 1.6 ppm as only one singlet even at –60 °C, in spite of the asymmetric nature of DAB^{IV} ligand. By contrast, in DAB^{I} and in its adduct [PtCl$_2$(DAB^{I})] the acac C-Me groups are clearly non-equivalent and appear as two separate singlets (Table III).

The coordination of the acac ligand to the copper center in [Cu(acac)(DAB^{IV})] is indicated by the nature of products of reaction 13:

$$\begin{array}{l} [\mathrm{Cu(acac)(DAB^{IV})}] \xrightarrow{+\mathrm{bipy(exc.)}} \\ \qquad [\mathrm{Cu(acac)(bipy)}]\mathrm{Cl} + \text{other products} \\ \qquad\qquad \Big\downarrow {+\mathrm{PPh_3}} \qquad (13) \\ trans\text{-}[\mathrm{PdCl\{C({=}NR)CMe{=}NR\}(PPh_3)_2}] \end{array}$$

(bipy = 2,2′-bipyridine)

The Cu(acac) unit is completely displaced from the DAB^{IV} ligand to yield the cationic compound [Cu(acac)(bipy)]Cl, which precipitates almost quantitatively from the reaction mixture. Subsequent treatment of the mother liquor with PPh$_3$ gives back the starting product of reactions 5–7. The complex [Cu(acac)(bipy)]Cl is a uni-univalent electrolyte in methanol and has a magnetic moment of 1.71 B.M. in dichloromethane, corresponding to the contribution of only one unpaired electron. A very close magnetic moment (1.76 B.M.) is also measured for the binuclear compound [Cu(acac)(DAB^{IV})]. The coordination geometry around the copper atom in these derivatives is approximately square-planar, as suggested by electronic (Fig. 2) and EPR spectroscopic data [13]:

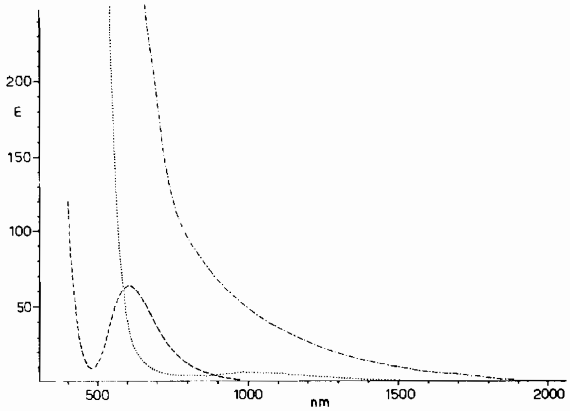


Fig. 2. Electronic spectra of [Cu(acac)(DAB^{IV})] in CH$_2$Cl$_2$ (—·—); [Cu(acac)(bipy)]Cl in MeOH (-----); [Ni(acac)(DAB^{IV})] in CH$_2$Cl$_2$ (·····) at the concentration of 8.57 g/l (molar extinction coefficients calculated for 9.75 × 10^{-3} *M* solution, by assuming a molecular weight corresponding to monomeric species).

	g_x	g_y	g_z	A (G)
[Cu(acac)(DAB^{IV})]	2.05	2.00	2.24	170
[Cu(acac)(bipy)]Cl	2.06	2.01	2.24	170

The mononuclear compound [Cu(acac)(bipy)]Cl shows a d–d band in methanol with a maximum at 605 nm, typical for Cu(II) complexes with essentially square-planar geometries [14]. For [Cu(acac)(DAB^{IV})], any d–d band at wavelengths lower than 800 nm is masked by the intense metal-to-ligand charge-transfer absorptions. However, the absence of d–d bands around 1000 nm rules out any detectable contribution of pseudo-tetrahedral Cu(II) species [14]. A square-planar structure has been observed in many bis-chelate Cu(II) derivatives with a N$_2$O$_2$ donor atom set, such as bis(salicylaldiminate)copper(II) [5] and [Cu(C$_2$O$_4$)(bipy)] (C$_2$O$_4$ = oxalate anion) [15].

The Pd(II)/Cu(II) binuclear complex [Cu(acac)(DAB^{IV})] and the related derivatives, obtained upon reaction with equimolar amounts of strong mineral acids, are of interest as potential catalysts in the oxidation of olefins, a property that we are currently investigating.

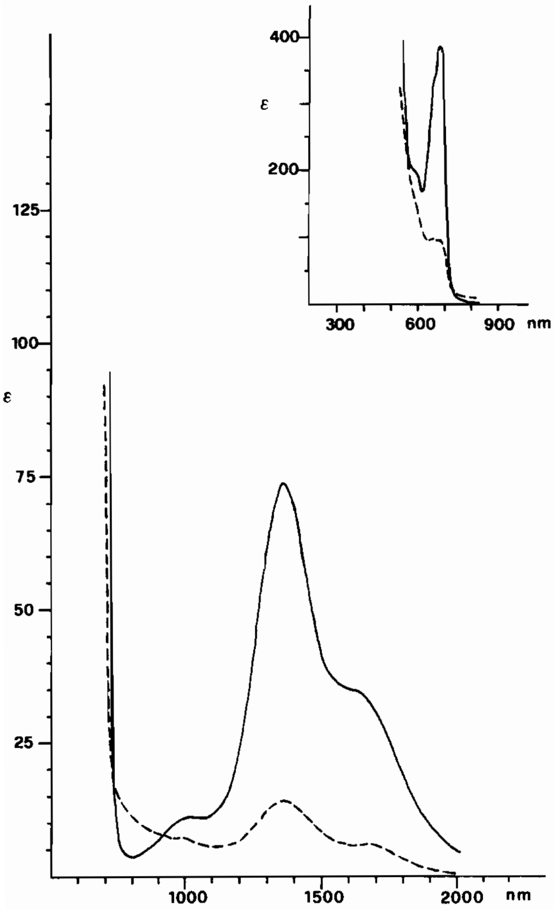


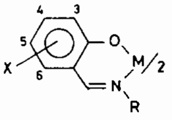
Fig. 3. Electronic spectra of $[CoCl_2(DAB)]$ in CH_2Cl_2 (——); $[Co(acac)(DAB^{IV})]$ in CH_2Cl_2 (-----) at the concentration of 8.79 g/l (molar extinction coefficients calculated for 10^{-2} M solution, by assuming a molecular weight corresponding to monomeric species.

The magnetic moments of $[M(acac)(DAB^{IV})]$ in the solid (M = Co, 4.34 B.M.; M = Ni, 3.22 B.M.) are usual for paramagnetic high-spin compounds with three and two unpaired electrons respectively, whereas they are considerably lower in dichloromethane solutions (for a 10^{-2} M concentration calculated by assuming a molecular weight corresponding to monomeric species: M = Co, 3.75 BM; M = Ni, 2.05 BM). On the other hand, from the electronic spectra in dichloromethane at comparable concentrations (Figs. 2 and 3) it appears that the contribution of high-spin pseudo-tetrahedral species is markedly reduced. For $[Ni(acac)(DAB^{IV})]$ (Fig. 2), only a weak, broad absorption at *ca.* 1000 nm is observed, which may be due either to octahedral associated species [16] or to a small amount of pseudo-tetrahedral monomer. As a matter of fact, pseudo-tetrahedral monomeric 1/1 adducts between $NiCl_2$ and 1,2-bis(imino)propyl–palladium(II) ligands are characterized by d–d bands in the range 1100–1000 nm with molar extinction coefficients of 50–60 cm^{-1} M^{-1} [17]. The spectrum of $[Co(acac)(DAB^{IV})]$ is reported in Fig. 3, together with that of the high-spin tetrahedral complex $[CoCl_2(DAB)]$ (μ_{eff} = 4.58 B.M. in dichloromethane, see Experimental). As can be inferred from the type and intensity of the d–d bands, a tetrahedral species is present also in $[Co(acac)(DAB^{IV})]$, but at considerably lower concentration.

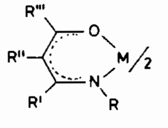
The particular behaviour of $[M(acac)(DAB^{IV})]$ (M = Co, Ni) in solution may be accounted for by the establishment of the following equilibria:

$$\begin{tikzcd}
\text{Associated species (high-spin)} \arrow[rr, shift left] \arrow[dr, shift left] & & \text{Tetrahedral monomers (high-spin)} \arrow[ll, shift left] \arrow[dl, shift left] \\
& \text{Square-planar monomers (low-spin)} \arrow[ul, shift left] \arrow[ur, shift left] &
\end{tikzcd} \quad (14)$$

Association in solution (and to a greater extent in the solid) probably occurs through O-bridges of the acac ligands, as was found for $[M_2(acac)_4L]$ and $[M_2(acac)_4L_2]$ derivatives (M = Co, Ni; L = N-donor ligand) [18]. For $[Ni(acac)(DAB^{IV})]$, the low-spin species is very likely a diamagnetic square-planar form, in line with the behaviour of nickel(II) bis-chelate complexes with N_2O_2 donor atoms, such as the bis(salicylaldiminate) and bis(β-chetoiminate) systems [5]:



C



D

(As an example, for complex C (M = Ni, X = 4-Me, R = i-Pr) the μ_{eff} values in the solid and in solution are 3.29 and 2.35 B.M., respectively).

In the case of $[Co(acac)(DAB^{IV})]$, the EPR spectrum shows the presence of a low-spin species (g = 2.00; A ≅ 15 G) which may be a square-planar monomer in equilibrium with a high-spin tetrahedral form, as was reported for complexes of type D with M = Co [5]. However, the available experimental evidence does not rule out a contribution of five-coordinate low-spin dimers similar to the O-bridged complex $[Co(Salen)]_2$ [19].

Reactions 10, 11 and 12 lead to the formation of binuclear compounds without exchange of ancillary ligands between the two metal centers. The 1,2-bis(imino)propyl group acts as a chelate ligand with a σ-N bonding mode, suggested by the down-field shift of δ(C-Me) signal upon coordination [11]. In the $PtCl_2$ adducts, this resonance is flanked by two ^{195}Pt satellites with a $^4J(Pt–H)$ value of 9 Hz. In the

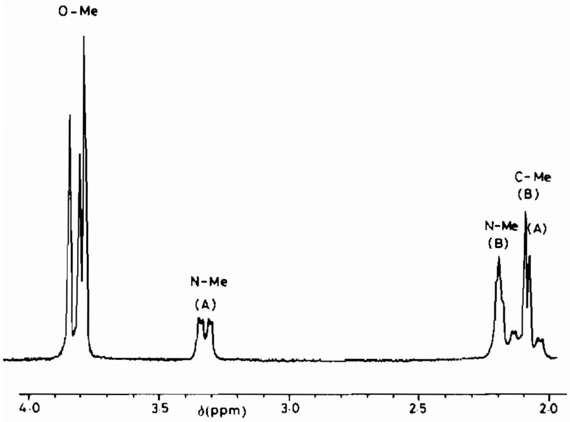


Fig. 4. ^{1}H NMR spectrum of $[PtCl_2(DAB^{III})]$ in the range 2.0–4.0 ppm; (A) signals of isomer A, (B) signals of isomer B.

far IR spectra, the coordinated MCl_2 group is characterized by two ν(M–Cl) vibrations in the ranges 346–311, 353–335 and 348–334 for M = Zn, Pd and Pt respectively, in good agreement with the corresponding frequencies in MCl_2 adducts of other 1,2-bis(imino)alkyl–palladium(II) derivatives [3, 17]. Further support to the proposed formulation is given also by the following reactions:

$$[ZnCl_2(DAB^{II})] + \text{bipy(exc.)} \longrightarrow [ZnCl_2(\text{bipy})] + DAB^{II} \qquad (15)$$

$$[PdCl_2(DAB^{III})] + 2PPh_3 \longrightarrow \textit{trans}\text{-}[PdCl_2(PPh_3)_2] + DAB^{III} \qquad (16)$$

$$[PtCl_2(DAB^{II})] + \text{dppe} \longrightarrow [PtCl_2(\text{dppe})] + DAB^{II} \qquad (17)$$

(dppe = 1,2-bis(diphenylphosphino)ethane)

The ligands DAB^{II} and DAB^{III} are quantitatively displaced from their adducts and can be recovered in high yield from the reaction mixtures (see Experimental).

Attempts to promote migration of ancillary ligands in the MCl_2 binuclear compounds by prolonged heating in acetonitrile (as in the case of the second step of reaction 4) failed or led to decomposition of the starting products.

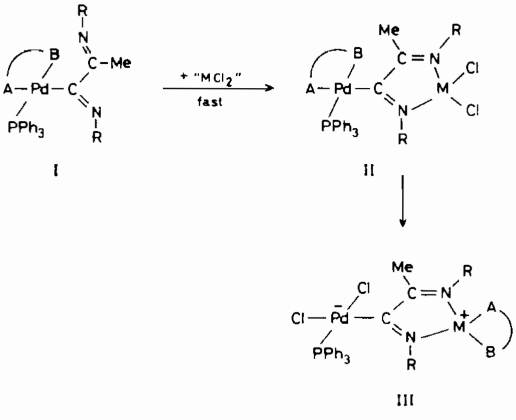
The δ(N=C–H) and δ(N-Me) signals and the ^4J(P–H) coupling constants of DAB^{II} are little affected by the coordination of the 1,2-bis(imino)propyl group [small down-field shifts with concomitant slight increase of ^4J(P–H)], suggesting that the configuration around the Pd atom of DAB^{II} is retained in its MCl_2 adducts.

The geometrical isomers A and B, initially present in free DAB^{III}, are observed also in the binuclear derivatives $[MCl_2(DAB^{III})]$ with different A/B ratios depending on the metal M: A/B = ½, ¼ and 1/1.5 for M = Zn, Pd and Pt, respectively. The ^{1}H NMR spectrum of $[PtCl_2(DAB^{III})]$ in the range 2–4 ppm (Fig. 4) shows the different patterns of δ(N-Me) signals of the isomer A (3.32 ppm) and isomer B (2.18 ppm) due to the different ^4J(P–H) coupling constants (3.3 and ~1 Hz for *trans* and *cis* MeN–Pd–PPh$_3$ arrangements, respectively).

Proposed Mechanism of Migration

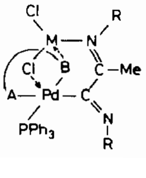
From the course of reactions 4 and 8–12 it appears that the easc of exchange of ancillary ligands depends essentially on the nature of M (no migration has so far been observed for M = Zn, whereas for M = Pt migration occurs only in the reaction with DAB [3]) and on the nature of the bidentate anionic ligand in the starting 1,2-bis(imino)propyl–palladium(II) complex. The latter influence is particularly evident in the reactions with $[PdCl_2(N{\equiv}CMe)_2]$, in which migration takes place with dmtc and acac groups, but it does not with the imino ligands Mesal and Mepyr.

Since the bidentate anions in the mononuclear complexes DAB–DAB^{III} do not undergo any relevant dissociation process, the mechanism of migration implies an interaction between the Pd and M metal centers in the reaction system, which may occur either *intermolecularly* without prior coordination of 'MCl_2' to the 1,2-bis(imino)propyl moiety, or *intramolecularly* in the stepwise reaction sequence 18:



(18)

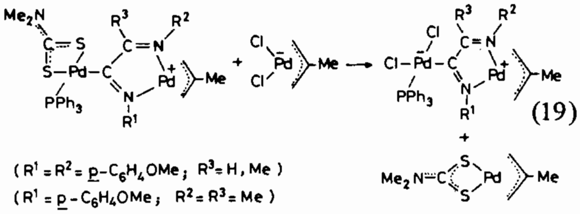
via opening and rearrangement of the five-membered α-diimino ring of II in a transition state of the type:



Although the mechanism involving an intermolecular ligand exchange between I and 'MCl_2' followed by coordination of the resulting M(A–B) species to the α-diimino group cannot be ruled out in the absence of kinetic data (unfortunately, in all the examined systems the migration rate was too high for a kinetic study by conventional spectrophotometric techniques), we are in favour of the intramolecular mechanism 18 on the basis of the following considerations:

i) An analogous stepwise process was observed in reaction 4 between DAB and $K[PtCl_3(CH_2{=}CH_2)]$.

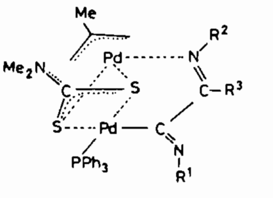
ii) A kinetic investigation of reaction 19:



(19)

($R^1 = R^2 = p\text{-}C_6H_4OMe$; $R^3 = H, Me$)
($R^1 = p\text{-}C_6H_4OMe$; $R^2 = R^3 = Me$)

has shown that the ligand exchange proceeds in two parallel steps k_1 and k_2, with the k_1 step corresponding to an intramolecular rearrangement of the cationic substrate in a transition state involving concerted α-diimino ring opening and migration of the bidentate anion [2]:



Under this scheme, the lack of ligand migration in the reactions 10–12, as well as in the reaction of DAB with $ZnCl_2$ [3], may be accounted for in terms of stabilization of the adducts II towards further rearrangement to the zwitterionic isomers III, resulting either from the formation of stable α-diimino cycles in II, or from the presence of stable Pd(A–B) chelate ring in the starting complexes I, or from the concomitance of both these factors. Thus, the markedly reduced tendency towards ligand migration in the reactions of DAB or DAB^{I} with $K[PtCl_3(CH_2{=}CH_2)]$, relative to the corresponding reactions with $[PdCl_2(N{\equiv}CMe)_2]$, is essentially related to a greater stability of α-diimino–Pt(II) five-membered cycles, as can be inferred from the relative values of dissociation constants in the complexes $[M(\eta^3\text{-}C_3H_5)(RN{=}CR'{-}CR'{=}NR)]^+$ ($R = p\text{-}C_6H_4OMe$; $R' = H, Me$; M = Pd, Pt) [20]. On the other hand, the reactivity trend observed in the reactions of DAB–DAB^{III} with $[PdCl_2(N{\equiv}CMe)_2]$ may be rationalized in terms of stronger chelating properties of the Mesal and Mepyr anions in DAB^{II} and DAB^{III}, respectively.

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